

forming greys by rotation were measured, and the results tabulated in percentages of the spectrum of white light and on a wave-length scale.

III. "The Conditions of the Evolution of Gases from Homogeneous Liquids." By V. H. VELEY, M.A., University College, Oxford. Communicated by A. VERNON HARCOURT, M.A., F.R.S. Received May 5, 1888.

(Abstract.)

This paper is conveniently divided into three parts. In part (i) an account is given of the effect of finely divided particles on the rate of evolution of gases resulting from chemical changes; in part (ii) the phenomenon of initial acceleration, as also the effect of variation of pressure on the evolution of gases, is discussed; in part (iii) the case of the decomposition of formic acid into carbonic oxide and water is investigated under constant conditions, other than those of the mass of reacting substances and of temperature.

Part I.—It is found that the addition of finely divided chemically inert particles increases the rate of evolution of gases from liquids in which they are being formed. The effect of these particles on the following chemical changes is investigated: (i) the decomposition of formic acid yielding carbonic oxide; (ii) the decomposition of ammonium nitrite in aqueous solution yielding nitrogen; (iii) the reduction of nitric acid into nitric oxide by means of ferrous sulphate; (iv) the decomposition of ammonium nitrate in a state of fusion producing nitrous oxide; and (v) the decomposition of potassium chlorate in a state of fusion producing oxygen. The finely divided substances used are pumice, silica, graphite, precipitated barium sulphate and glass-dust.

Part II.—It is observed that, conditions of temperature remaining the same, the rate of evolution of a gas from a liquid is at first slow, then gradually increases until it reaches a maximum and for some time constant rate. From this point the rate decreases proportionally to the diminution of mass. This is observed in the cases of the decomposition of formic acid, potassium ferrocyanide, and of oxalic acid by concentrated sulphuric acid, and in that of ammonium nitrate. It has previously been observed in the case of the decomposition of ammonium nitrite in aqueous solution. The same phenomenon repeats itself when the temperature is temporarily lowered and then raised to its former point, and also to a more marked degree when, temperature remaining the same, the superincumbent pressure is suddenly increased.

The reduction of pressure from one to a fraction of an atmosphere

produces no *permanent* effect on the rate of evolution of a gas from a liquid, a decrease of pressure, however, produces *temporarily* an increase in the rate, and an increase of pressure conversely produces *temporarily* a decrease in the rate.

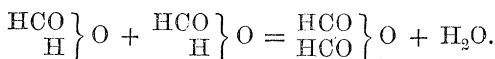
Part III.—The case of the decomposition of formic acid into carbonic oxide and water by diluted sulphuric acid is studied with the aid of an apparatus by means of which the temperature is kept constant within one-twentieth of a degree. It is shown that the rate of evolution of carbonic oxide is expressible by the following equation:—

$$\log(\tau + t) + \log r = \log c,$$

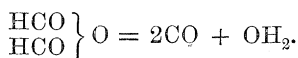
in which τ is the time from the commencement of the observations; t is the interval of time from the moment of commencement, and that at which, conditions remaining the same, the interval of time required for unit change would have been *nil*; r is the mass at the end of each observation, and c is a constant. The results calculated by this hypothesis agree with those observed, whether the interval of time required for unit change is 30 or 960 minutes. The curve expressing the rate of chemical change in terms of mass is thus hyperbolic and illustrative of the law

$$\frac{dr}{d\tau} = -\frac{r^2}{c},$$

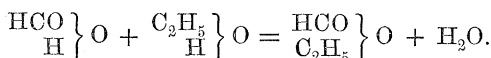
which expresses the rate at which equivalent masses act upon another; $1/c$ in each experiment is the amount of each unit mass which reacts with the other per unit of time, when an unit mass of each substance is present. Since then equivalent masses take part in the change, it is reasonable to suppose that at first an anhydride of formic acid is produced thus:—



The anhydride is unstable, and is subsequently decomposed into carbonic oxide and water,



The change may thus be compared to the production of ethyl formate from formic acid and alcohol,



with which it shows several points of analogy.

In the original paper the methods of observation and the apparatus used are described in full, and the results obtained are set forth in a series of tables.